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Dewar lactone as a modular platform to a new class of substituted poly(acetylene)s†

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A variety of 3-substituted-4-halocyclobutenes originating from Dewar lactone (2-oxabicyclo[2.2.0]hex-5-en-3-one) were synthesized and polymerized using the Hoveyda–Grubbs 2nd generation catalyst. The polymerization reactions were found to proceed in a controlled manner, which provided a means to tune polymer molecular weight and to effect chain extensions. Treating the polymers with an organic base (*e.g.*, triethylamine) facilitated elimination and afforded the corresponding substituted poly(acetylene)s which featured substituents on every four carbon atoms along the polymer backbone. The polymers were characterized using gel permeation chromatography and a variety of different spectroscopic techniques (*i.e.*, NMR, FT-IR, UV-vis, and Raman). The physical, chemical, and electronic properties of the polymers were found to be dependent on the pendant substituents.

Introduction

Polymers possessing π-conjugated backbones continue to attract significant attention in part because they can enable a variety of contemporary electronic devices,[1–4] including light emitting diodes,[5–7] solid-state lasers,[8] organic field effect transistors,[9] photovoltaics,[10–12] and chemical sensors.[13,14] The prototypical example of a conjugated polymer is poly(acetylene). Although the earliest reports on the synthesis of poly(acetylene) date back to the 1950s,[15–17] the polymeric material was not widely recognized as an organic conductor until 1977 when Shirakawa, Heeger, and MacDiarmid reported significant increases in conductivity upon doping with halogen vapors.[18,19] However, outstanding issues, including limited solubility[20] and a lack of catalysts that enable the controlled polymerization of acetylene and related monomers,[21,22] have prevented access to high molecular weights and hampered its utility in various applications. For example, while poly(acetylene) becomes insoluble when the chain length exceeds 10 repeat units,[20] enhanced intrinsic chemical or physical properties can be expected from high molecular weight derivatives;[23,24] thus, the development of methodology to access such materials is warranted.

The aforementioned insolubility challenges have been addressed in part through the formation of block copolymers wherein poly(acetylene) is linked to segments that render the entire material soluble (*e.g.*, poly(acetylene)-*block*-poly(*N*-cyclohexyl-*exo*-norbornene-5,6-dicarboximide))[25,26] or through the polymerization of soluble poly(acetylene) precursors followed by conversion to poly(acetylene) (*e.g.*, polymerization of benzvalene followed by isomerization using $HgCl_2$).[27,28] Despite these advances, compromised electronic properties and inadvertent crosslinking have impeded the widespread employment of such approaches. Recently, our group reported the polymerization of a derivative of Dewar benzene followed by an elimination–isomerization sequence to afford *trans*-poly(acetylene) in a well-controlled manner.[29] Although the methodology effectively overcomes some of the aforementioned challenges, the formation of block copolymers is required to enhance solubility.

Appending substituents to the backbone of poly(acetylene) in a manner that disrupts packing interactions and facilitates dissolution has been explored as an alternative approach to enhancing solubility (see Scheme 1).[30,31] For example, North and coworkers reported a cationic polymerization of phenylacetylene to yield polymers that were soluble in common organic solvents.[32] However, difficulties arose in controlling the polymerization reaction as charge delocalization was found to deactivate the propagating centers[33,34] and afforded multiple side products.[32] Similarly, the polymerization of propiolate esters often provides polymers with broad polydispersity index (*Đ*) values, uncontrolled molecular weights and low yields.[35,36] In some cases, the side groups introduce steric

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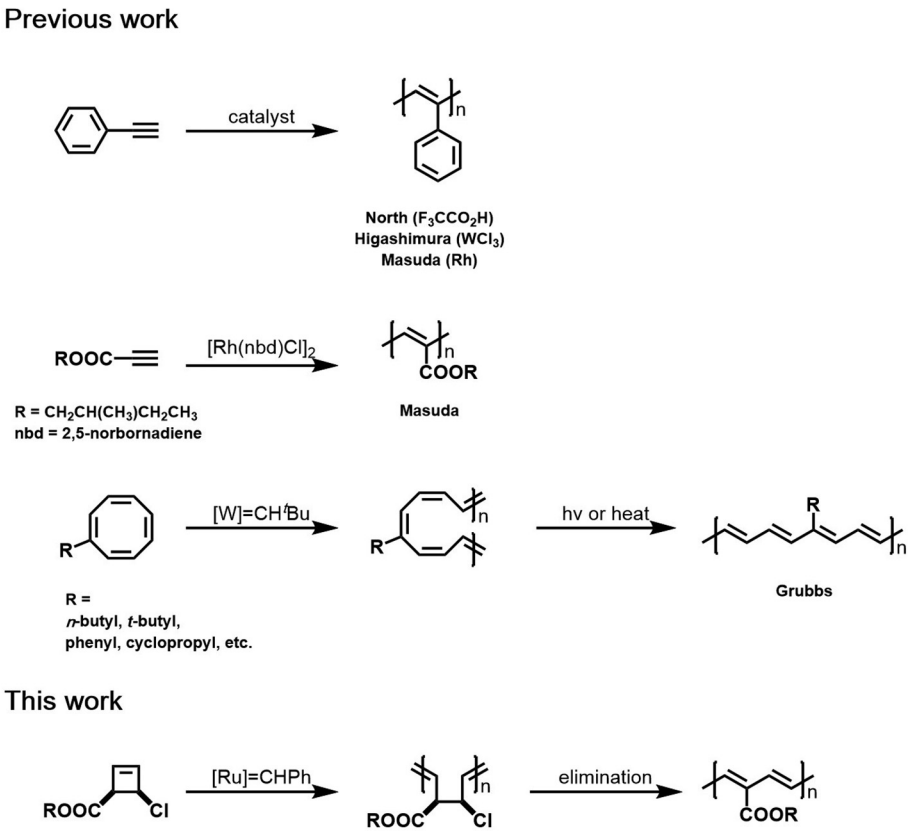


Scheme 1 Selected examples of routes that may be used to synthesize substituted poly(acetylene)s.

interactions that promote twisting of the polymer chains in a manner that interrupts conjugation along the backbone.[37–41]

A different method for synthesizing substituted poly(acetylene)s was disclosed by Grubbs and coworkers. Using ring-opening metathesis polymerization (ROMP), a substituted 1,3,5,7-cyclooctatetraene (COT)[31] was used to prepare derivatives of poly(acetylene) that featured repeat units with up to one pendant functional group per eight carbon atoms.[31,42–44] Although the polymers were found to be soluble in organic solvents,[31] control over the polymerization reaction was challenged by the low ring strain of the monomer and competing secondary metathesis reactions.[45] Similar to its (unsubstituted) parent,[46] the ROMP of the substituted COTs resulted in backbiting and thus extruded benzene and its substituted derivative[31] in a manner that lowered the yield of the reaction and broadened the distribution of polymer chains produced. The extrusion of substituted benzene appeared to be preferred over benzene, which reduced the solubility of some of the poly (acetylene) derivatives that were prepared using the methodology.

To access substituted poly(acetylene)s in a manner that is controlled and minimizes side reactions, we envisioned the ROMP of a series of alkyl 4-chlorocyclobut-2-ene-1-carboxylates followed by a post-polymerization elimination. The monomers may be readily accessed from Dewar lactone and can be expected to undergo rapid polymerization in a controlled fashion with minimal backbiting due to the high ring-strain of four membered rings.[47–49] Moreover, since the halogen leaving group is proximal to a carbonyl group, the post-polymerization modification reaction was anticipated to occur under mild conditions and afford soluble poly(acetylene) derivatives with substituents on every fourth carbon of the polymer repeat unit.

Experimental

Materials

Unless otherwise noted, all manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. Methanol and ethanol were purchased from Daejung Chemicals & Metals. 2,2,2-Trifluoroethanol, the Grubbs 1st generation (G1) catalyst, the Grubbs 2nd generation (G2) catalyst and the Hoveyda–Grubbs 2nd generation (HG2) catalyst were purchased from Sigma-Aldrich. The Grubbs 3rd generation (G3) catalyst was generated from the Grubbs 2nd generation (G2) catalyst by following previously reported procedures.[50] 2-Ethylhexyl alcohol was purchased from Acros Organics. Coumalic acid, a hydrogen chloride solution (2.0 M in Et_2O), oxalyl chloride, *N*,*N*′-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), benzyl alcohol, potassium hydroxide and ethyl vinyl ether were purchased from Alfa-Aesar.

Instrumentation and characterization

Solvents were dried and sparged with nitrogen using a VAC Atmospheres solvent purification system. ^{1}H and ^{13}C NMR spectra were recorded in CD_2Cl_2 (^{1}H: 5.32 ppm; ^{13}C: 53.8 ppm), $CDCl_3$ (^{1}H: 7.26 ppm; ^{13}C: 77.2 ppm) or CD_3OD (^{1}H: 3.31, 4.87 ppm; ^{13}C: 49.0 ppm) using Bruker 400 MHz and 100 MHz spectrometers, respectively. ^{19}F NMR spectra were recorded in CD_2Cl_2 using a Bruker 377 MHz spectrometer and calibrated to C_6F_6 (−162.61 ppm; internal standard).[51] Coupling constants (J) are expressed in hertz (Hz). Splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad; bd, broad doublet; bt, broad triplet; bm, broad multiplet. High-resolution mass spectra (HR-MS) were obtained using a JMS-T100LP AccuTOF LC-plus 4G Atmospheric Pressure Ionization High Resolution Time-of-Flight Mass Spectrometer (Waters, Inc.) Gel permeation chromatography (GPC) was performed on a Malvern GPCmax Solvent/Sample Module system. THF was used as the eluent at a flow rate of 0.8 mL min^{-1}. Attenuated total reflection (ATR) spectra were recorded on an Agilent Cary-630 FT-IR spectrometer. Raman spectra were recorded on a WITec alpha 300M confocal Raman microscope. Specific rotations were determined using a Kruss P3000 Optronic polarimeter. Measurements were taken in a quartz cell with a path length of 50 mm and at a wavelength of 589 nm. Thermogravimetric analyses (TGA) were performed on a Thermal Advantages (TA) Q500 at a heating rate of 10 °C min^{-1} under an atmosphere of nitrogen. Differential scanning calorimetry (DSC) was performed on a Thermal Advantages Q2000 at heating and cooling rates of 20 °C min^{-1} under an atmosphere of nitrogen. Elemental analyses were performed using a ThermoScientific Flash 2000 Organic Elemental Analyzer that was calibrated with 2,5-bis(5-*tert*-butyl-benzoxazol-2-yl)thiophene. X-ray photoelectron spectroscopy were performed using an Escalab 250Xi (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a monochromated aluminum Kα source (1486.6 eV). UV-vis spectroscopy data were recorded using an Agilent Cary 100 UV-visible Spectrometer. An Ace photochemical reactor (medium pressure Hg, 450 W) was used as a light source. pK_a predictions were calculated using MarvinSketch 19.13. Further details regarding the measurement conditions and procedures can be found in the ESI.†

Synthesis of 2*H*-pyran-2-one (3)

Coumalic acid (**2**) (20.0 g, 143 mmol) was placed in the capped end of a quartz tube while the open end of the tube was loosely packed with strips of copper foil. The quartz tube was inserted into a horizontal furnace and evacuated (0.05 mbar). The furnace was then gradually heated to 650 °C for 1 h. Once the furnace temperature reached the target temperature, the capped end of quartz tube was wrapped with heating tape and heated to 195 °C. Subsequent sublimation of **2** followed by pyrolysis afforded **3** which was collected as a liquid in a cold trap cooled using liquid nitrogen. After the reaction, crude **3** was purified by column chromatography using a mixture of ethyl acetate (EtOAc) and *n*-hexane (3 : 1 v/v) as an eluent followed by distillation (95 °C, 20 mbar) to afford **3** (9.6 g, 100 mmol) as a colorless liquid in 70% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.40–7.54 (m, 1H), 7.25–7.37 (m, 1H), 6.26–6.38 (d, 1H, J = 9.4 Hz), 6.11–6.25 (t, 1H, J = 6.3 Hz). Spectral data agreed with literature values.[52]

Synthesis of 2-oxabicyclo[2.2.0]hex-5-en-3-one (4)

Compound **3** (4.0 g, 41.6 mmol) was dissolved in anhydrous Et_2O (1.0 L), and then placed into jacketed photoreactor vessel under positive nitrogen flow and cooled to −15 °C. A separate glass inner-well which houses the medium pressure mercury lamp was also cooled to −15 °C prior to photo-irradiation. The photochemical reaction proceeded for four days, as monitored by ^{1}H NMR spectroscopy. Afterward, the residual solution was concentrated under reduced pressure at −15 °C. By integrating ^{1}H NMR signals attributed to **4** to those assigned to the residual solvent, the concentration of the crude product was determined to be approximately 5.5 M in Et_2O. The concentrated solution was directly used for the synthesis of compound **5** without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.72–6.88 (m, 1H), 6.50–6.69 (m, 1H), 5.28–5.41 (m, 1H), 4.33–4.51 (s, 1H). Spectral data agreed with literature values.[53]

Synthesis of (*rac*)-*cis*-4-chlorocyclobut-2-ene-1-carboxylic acid (5)

A concentrated Et_2O solution of **4** (11 mL, *ca.* 5.5 M) was injected into a mixture of Et_2O (1.0 L) and 5.0 g of molecular sieves (3.0 Å) under an atmosphere of nitrogen. The solution was cooled to −10 °C, upon which an ethereal solution of hydrogen chloride (2.0 M, 83.2 mL, 166.4 mmol) was slowly added. The reaction proceeded for 24 h at −10 °C and was then filtered to remove the molecular sieves. Diethyl ether was then subsequently removed under reduced pressure at 10 °C and the resulting product was purified *via* column chromatography using CH_2Cl_2 as an eluent to afford 2.8 g of the desired product as a white solid in 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.42–11.05 (br, 1H), 6.11–6.38 (m, 2H), 4.92–5.18 (d, 1H, J = 4.3 Hz), 4.05–4.21 (d, 1H, J = 4.3 Hz). Spectral data agreed with literature values.[54]

General procedure A

Dimethylformamide (DMF) (58 μL, 0.75 mmol) was added to a solution of **5** (0.5 g, 3.77 mmol) in CH_2Cl_2 (25.1 mL) at 0 °C under an atmosphere of nitrogen. Oxalyl chloride (0.49 mL, 5.66 mmol) was then added dropwise and the reaction was allowed to proceed for 1 h. Afterward, the residual solvent was removed under reduced pressure (25 °C, 50 mbar). The residue was re-dissolved in CH_2Cl_2 (25.1 mL), and then the solution was charged with the alcohol (2.0 equiv.) that corresponded to the desired derivative. The reaction was allowed to proceed for 12 h at room temperature under an atmosphere of nitrogen. Excess solvent was then removed under reduced pressure (10 °C, 100 mbar). The crude products were purified by column chromatography using a mixture of CH_2Cl_2 and *n*-hexane (1 : 2 v/v) as an eluent. With the exception of **1c**, products **1a–d** were obtained as their racemates as determined by polarimetry.

Synthesis of (*rac*)-*cis*-methyl 4-chlorocyclobut-2-ene-1-carboxylate (1a)

General procedure A and methanol afforded the desired product as a colorless liquid (0.30 g, 54% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.19–6.30 (m, 2H), 5.04–5.15 (d, 1H, J = 4.3 Hz), 4.02–4.11 (d, 1H, J = 4.3 Hz), 3.71 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 170.6, 140.8, 137.3, 57.1, 54.6, 52.4. HR-MS (ESI) calcd for $C_6H_7ClO_2$ $[M + H]^+$ 147.0213, found 147.0217.

Synthesis of (*rac*)-*cis*-ethyl 4-chlorocyclobut-2-ene-1-carboxylate (1b)

General procedure A and ethanol afforded the desired product as a colorless liquid (0.36 g, 60% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.17–6.34 (m, 2H), 5.03–5.15 (d, 1H, J = 4.3 Hz), 4.09–4.28 (m, 2H), 3.96–4.10 (d, 1H, J = 4.3 Hz), 1.19–1.34 (t, 3H, J = 7.1 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2): 170.2, 140.7, 137.4, 61.5, 57.2, 54.6, 14.7. HR-MS (ESI) calcd for $C_7H_9ClO_2$ $[M + H]^+$, 161.0364, found 161.0369.

Synthesis of *cis*-2-ethylhexyl 4-chlorocyclobut-2-ene-1-carboxylate (1c)

General procedure A and 2-ethylhexyl alcohol afforded the desired product as a colorless liquid (0.50 g, 54% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.16–6.35 (m, 2H), 5.04–5.16 (d, 1H, J = 4.3 Hz), 3.91–4.11 (m, 3H), 1.52–1.66 (m, 1H), 1.21–1.49 (m, 8H), 0.74–0.99 (t, 6H, J = 7.4 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 170.4, 140.6, 137.4, 67.8, 57.2, 54.8, 39.4, 30.9, 29.5, 24.3, 23.6, 14.4, 11.3. HR-MS (ESI) calcd for $C_{13}H_{21}ClO_2$ $[M - H]^+$ 243.1146, found 243.1151. $[\alpha]_D^{22}$ −0.28° (c 1.2, CH_2Cl_2).

Synthesis of (*rac*)-*cis*-benzyl 4-chlorocyclobut-2-ene-1-carboxylate (1d)

General procedure A and benzyl alcohol afforded the desired product as a colorless liquid (0.47 g, 56% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.25–7.46 (m, 5H), 6.20–6.33 (m, 2H), 5.06–5.25 (d, 3H, J = 4.3 Hz), 4.04–4.19 (d, 1H, J = 4.3 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 170.1, 140.9, 137.2, 136.5, 129.0, 128.8, 67.3, 57.2, 54.6. Spectral data agreed with literature values.[54]

Synthesis of (*rac*)-*cis*-2,2,2-trifluoroethyl 4-chlorocyclobut-2-ene-1-carboxylate (1e)

Compound **5** (0.2 g, 1.5 mmol) was dissolved in CH_2Cl_2 (3.0 mL) followed by the addition of a catalytic amount of DMAP (3.0 mg, 0.02 mmol) and 2,2,2-trifluoroethanol (0.34 mL, 4.5 mmol) at 0 °C under an atmosphere of nitrogen. The resulting solution was then charged with *N*,*N*′-dicyclohexylcarbodiimide (DCC) (0.34 g, 1.65 mmol) and allowed to reach room temperature. The reaction mixture was stirred under an atmosphere of nitrogen for 3 h, filtered to remove the urea byproduct and then evaporated under reduced pressure (10 °C, 100 mbar). The crude material was then purified by column chromatography using a mixture of CH_2Cl_2 and *n*-hexane (1 : 3 v/v) as an eluent to afford the desired product as a colorless liquid (0.2 g, 62% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.20–6.35 (m, 2H), δ 5.07–5.20 (d, 1H, J = 4.3 Hz), δ 4.44–4.65 (m, 2H), δ 4.13–4.27 (d, 1H, J = 4.3 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 160.8, 141.5, 136.5, 125.0, 122.3, 61.3, 56.8. ^{19}F NMR (377 MHz, CD_2Cl_2): δ −73.9 (s). HR-MS (ESI) calcd for $C_7H_6ClF_3O_2$ $[M - Cl]^+$ 179.0314, found 179.0300.

General procedure B

Compound **1** (1.0 mmol) and CH_2Cl_2 (1.5 mL) were added to an air-free reaction flask (10 mL) at room temperature under a positive flow of nitrogen. A solution of HG2 (7.7 mg, 1.22 mol%) in anhydrous CH_2Cl_2 (0.4 mL) was then injected and the mixture was gently stirred for 1 h at room temperature. The reaction was quenched upon the addition of ethyl vinyl ether (0.1 mL) and the resulting mixture was poured into cold hexane (*ca.* 100 mL). The polymeric material that precipitated was subsequently collected, dried under reduced pressure, and then characterized.

Synthesis of poly(1a)

General procedure B and **1a** (0.15 g, 1.0 mmol) afforded the desired product as a pale green powder (104 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.44–6.04 (br, 2H), 4.48–5.26, 3.23–3.51 (br, 2H), 3.55–3.92 (br, 3H).

Synthesis of poly(1b)

General procedure B and **1b** (0.16 g, 1.0 mmol) afforded the desired product as a white powder (126 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.45–6.08 (br, 2H), δ 4.48–5.36 (br, 1H), δ 3.92–4.38 (br, 2H), δ 3.08–3.92 (br, 1H), δ 0.99–1.36 (br 3H).

Synthesis of poly(1c)

General procedure B and **1c** (0.24 g, 1.0 mmol) afforded the desired product as a brown oil (215 mg, 88% yield). Note: The high solubility of poly(**1c**) prevented precipitation and thus the material was purified by passing a CH_2Cl_2 solution of the polymer through acidic alumina. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.41–6.04 (br, 2H), δ 4.49–5.27 (br, 1H), δ 3.86–4.22 (br, 2H), δ 3.19–3.85 (br, 1H), δ 1.45–1.79 (br, 1H), δ 1.02–1.44 (br, 8H), δ 0.63–1.02 (br, 6H).

Synthesis of poly(1d)

General procedure B and **1d** (0.22 g, 1.0 mmol) afforded the desired product as a pale brown powder (206 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03–7.40 (br, 5H), δ 5.40–5.99 (br, 2H), δ 4.41–5.33(br, 3H), δ 3.10–3.96 (br, 1H).

Synthesis of poly(1e)

General procedure B and **1e** (0.21 g, 1.0 mmol) afforded the desired product as a pale brown powder (193 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.37–6.20 (br, 2H), δ 4.25–5.27 (br, 3H), δ 3.34–3.98 (br, 1H). ^{19}F NMR (377 MHz, CD_2Cl_2): δ −74.1 (s).

General procedure C

A mixture of 50 mg of poly(**1a–e**) in THF (50 mL) was treated with Et_3N (10 equiv. based on the repeat unit of the polymer).

After stirring the resulting mixture for 5 h at 30 °C under air, the residual solution was concentrated under reduced pressure and the polymer solution was then poured into excess methanol. The precipitated solids were collected and dried to afford the desired products (**7a–e**).

Synthesis of 7a

General procedure C and poly(**1a**) afforded the desired product as a dark red solid (30 mg, 80% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.50–8.46 (br, 3H), δ 3.29–4.08 (br, 3H).

Synthesis of 7b

General procedure C and poly(**1b**) afforded the desired product as a dark red solid (29 mg, 76% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.49–8.33 (br, 3H), δ 3.90–4.47 (br, 2H), δ 0.89–1.47 (br, 3H).

Synthesis of 7c

General procedure C and poly(**1c**) afforded the desired product as a dark red gel (39 mg, 91% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.38–8.05 (br, 3H), δ 3.64–4.27 (br, 2H), δ 1.59–1.76 (br, 1H), δ 1.04–1.46 (br, 8H), δ 0.67–1.01 (br, 6H).

Synthesis of 7d

General procedure C and poly(**1d**) afforded the desired product as a dark red solid (41 mg, 98% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.96–7.60 (br, 5H), δ 4.73–5.50 (br, 2H).

Synthesis of 7e

General procedure C and poly(**1e**) afforded the desired product as a dark red solid (30 mg, 73% yield). Note: the polymer was precipitated from distilled water in lieu of methanol. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.37–6.20 (br, 2H), 4.25–5.27 (br, 3H), 3.34–3.98 (br, 1H). ^{19}F NMR (377 MHz, CD_2Cl_2): δ −74.0 (s).

Synthesis of 7f from poly(1d)

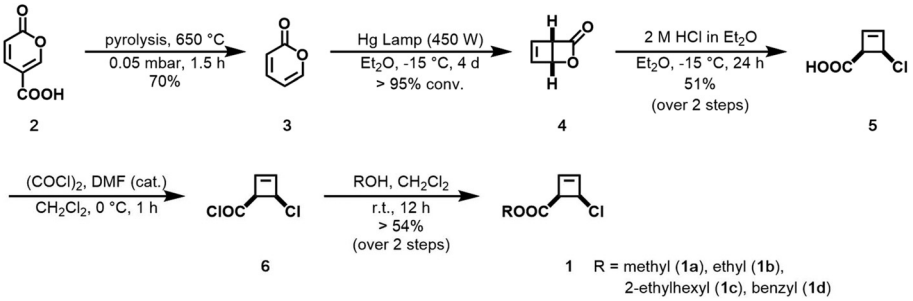
A solution of 0.4 g of potassium hydroxide (7.2 mmol, 40.0 equiv. based on the repeat unit of the polymer) dissolved in H_2O (4.0 mL) was added to a solution of 40 mg of poly(**1d**) (0.18 mmol based on the repeat unit) in THF (1.0 mL). Although two phases were initially observed, a single phase formed upon stirring. After allowing the reaction to proceed for 12 h at 30 °C under air, the residual solvent was concentrated under reduced pressure and poured into an excess quantity of aqueous HCl (pH ~ 4). The precipitated solids were collected *via* centrifugation and then dried under reduced pressure to afford the desired product as a dark red solid (13 mg, 75% yield). ^{1}H NMR (400 MHz, CD_3OD): δ 6.0–8.0 (br).

Synthesis of 7f using poly(1e)

A solution of 45 mg of lithium hydroxide (1.88 mmol, 8.2 equiv. based on the repeat unit of the polymer) in H_2O (1.0 mL) was added to a solution of 50 mg of poly(**1e**) (0.23 mmol based on the repeat unit) in THF (3.0 mL). Although two phases were initially observed, a single phase formed upon stirring. After allowing the reaction to proceed for 12 h at 30 °C under air, the residual solvent was concentrated under reduced pressure and poured into an excess quantity of aqueous HCl (pH ~ 4). The precipitated solids were collected *via* centrifugation and then dried under reduced pressure to afford the desired product as a dark red solid (12 mg, 55% yield). Spectral data agreed with the data recorded for **7f**.

Results and discussion

The synthetic route used to prepare **1** was adapted from reported procedures[53–55] and is summarized in Scheme 2. Briefly, pyrolysis of coumalic acid (**2**) (650 °C, 0.05 mbar) followed by column chromatography and distillation (95 °C, 20 mbar) afforded **3** as a colorless liquid in 70% yield. A photochemical isomerization reaction was then performed in diethyl ether at −15 °C and monitored by analyzing aliquots removed from the mixture using ^{1}H NMR spectroscopy until the transformation reached completion (*ca.* four days). The residual solution was removed under reduced pressure at −15 °C to give crude **4**, which was used directly in the next step without further purification. Dropwise addition of an ethereal solution of hydrochloric acid (2 M) to an anhydrous diethyl ether solution of **4** followed by stirring at −10 °C for 24 h provided **5**, which was subsequently purified by column chromatography to afford a white solid product in 51% yield over two steps. Addition of oxalyl chloride and DMF to **5** in CH_2Cl_2 followed by stirring for 1 h gave the acid chloride **6**. After removal of excess oxalyl chloride and CH_2Cl_2 under reduced pressure



Scheme 2 Synthetic procedure used to prepare various *cis*-4-chlorocyclobut-2-ene-1-carboxylic esters (**1**).

(25 °C, 50 mbar), the residual crude product (**6**) was re-dissolved in CH_2Cl_2 and introduced to an alcohol (*i.e.*, methanol, ethanol, 2-ethylhexanol or benzyl alcohol). The esterification reaction required 12 h to afford the corresponding products (**1a**, **1b**, **1c**, or **1d**, respectively), which were isolated by column chromatography in yields that ranged from 54 to 60%. A 2,2,2-trifluoroethyl derivative (**1e**) was prepared using a Steglich esterification reaction,[56] wherein 2,2,2-trifluoroethanol and a catalytic amount of DMAP were dissolved in a minimal amount of CH_2Cl_2 and then treated with **5** followed by *N*,*N*′-dicyclohexylcarbodiimide (DCC). The urea side product was removed *via* filtration and the resulting crude product was purified by column chromatography to afford **1e** in 62% yield.[57]

With **1** in hand, polymerization efforts commenced using the 2-ethylhexyl derivative (**1c**) as the polymer obtained from this monomer was predicted to exhibit a relatively high solubility and thus facilitate characterization. To our surprise, the Grubbs 3rd generation (G3) catalyst was found to be ineffective at converting **1c** to its respective polymer (*vide infra*); as such, efforts were re-directed toward using the Hoveyda–Grubbs 2nd generation (HG2) catalyst. Introducing a CH_2Cl_2 solution of the monomer ($[\mathbf{1c}]_0$ = 0.2 M) to the catalyst ($[\mathbf{1c}]_0/[HG2]_0$ = 82) for 1 h under an atmosphere of nitrogen followed by the addition of ethyl vinyl ether (0.1 mL) to quench the reaction afforded a polymer, as determined by the observation of broad signals in the ^{1}H NMR spectrum recorded for the material. The polymer was purified by filtration of the crude reaction mixture through acidic alumina followed by removal of the residual solvent and subsequently collected in 88% yield based on the structure of poly(**1c**). Using gel permeation chromatography (GPC), the number average molecular weight (M_n) of the polymer (24.9 kDa) was found to be in good agreement with the theoretical value (20.0 kDa) and the polydispersity index ($Đ$) of the material was measured to be relatively low (1.17). Comparing the ^{1}H NMR spectra recorded for the monomer to its corresponding polymer revealed an upfield shift of the olefinic signals assigned to the cyclobutenyl moiety (6.10–6.38 ppm; $CDCl_3$) upon polymerization (5.5–6.1 ppm; $CDCl_3$).

Next, efforts were directed toward determining if the aforementioned polymerization reaction was controlled. As shown in Fig. 1a, GPC revealed that after the initial monomer feed ($[\mathbf{1c}]_0/[HG2]_0$ = 61) was consumed, an increase in molecular weight was observed when additional **1c** ($[\mathbf{1c}]_{TOT}/[HG2]_0$ = 122) was added (*cf.*, M_n = 13.9 kDa *vs.* M_n = 25.9 kDa) while the $Đ$ values remained low (<1.2). Moreover, the experimentally determined molecular weights agreed with their theoretical values (15 kDa and 30 kDa, respectively). These observations indicated that the growing polymer chains remained active and that chain transfer was minimal over the course of the sequential polymerization reactions. In a separate set of experiments, a linear relationship between the initial monomer-to-catalyst feed ratio and the GPC-determined M_n values for the polymers was observed (Fig. 1b). Moreover, the experimentally derived molecular weights of the polymers generally agreed with their theoretical values. The polymers also exhibited low polydispersity values ($Đ$ = 1.23 to 1.32) and were obtained in high yields (>88%). Based on these results, we concluded that the polymerization of monomer **1c** using HG2 was controlled and afforded well-defined polymers with tunable molecular weights.

As summarized in Table 1, similar outcomes were achieved when analogous polymerization reactions were performed with most of the other derivatives of **1**. Monomer **1e** proved to be an exception as the corresponding polymer was determined to exhibit a relatively large polydispersity value ($Đ$ = 1.64) and a molecular weight (M_n = 7.3 kDa) that deviated from the theoretical value (3.2 kDa). We surmised that the 2,2,2-trifluoroethyl substituent withdraws electron density from the carbonyl group in a manner that deactivates the catalyst and inhibits the polymerization reaction (*vide infra*). Despite the synthetic drawback, poly(**1e**) was envisioned as a precursor to a water-soluble derivative of poly(acetylene) and thus was further studied, as described in more detail below.

With poly(**1**) in hand, efforts were directed toward transforming the polymers into their poly(acetylene) derivatives (Scheme 3). As part of an initial set of experiments, an excess amount of TEA (10 equiv. based on the repeat unit of the

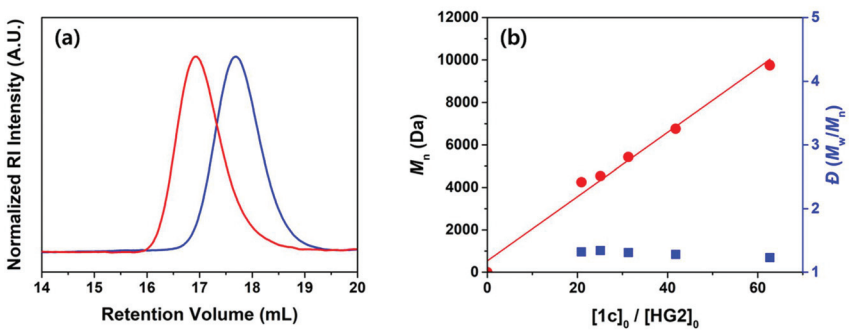
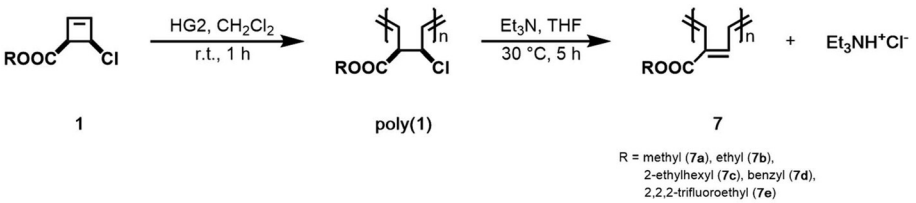


Fig. 1 (a) Representative gel permeation chromatograms recorded for poly(**1c**) (blue) and its chain extended polymer (red). Conditions: $[\mathbf{1c}]_0/[Ru]_0$ = 61, CH_2Cl_2; M_n = 13.9 kDa, $Đ$ = 1.19 (blue); additional **1c** was added after 1 h: ($[\mathbf{1c}]_0$ + $[\mathbf{1c}]_1$)/$[Ru]_0$ = 122, CH_2Cl_2, M_n = 25.9 kDa, $Đ$ = 1.18 (red). (b) Plot of M_n (red circles) and $Đ$ (blue squares) values *versus* different $[\mathbf{1c}]_0$ to $[HG2]_0$ feed ratios. Conditions: $[\mathbf{1c}]_0$ = 0.20 M, CH_2Cl_2, 1 h, room temperature. Isolated yields were typically >88%.

Table 1 Summary of data collected for poly(**1a–1e**)[a]

Polymer	$M_{n\ exp.}$[b] (kDa)	$M_{n\ theory}$[c] (kDa)	$[M]_0/[C]_0$[d]	DP[e]	$Đ$[b]	Conversion[f] (%)	Yield[g] (%)
Poly(**1a**)	15.7	20.0	136	107	1.24	>99	71
Poly(**1b**)	21.5	20.0	125	134	1.18	>99	79
Poly(**1c**)	24.9	20.0	82	102	1.17	>99	88[h]
Poly(**1d**)	24.2	20.0	90	109	1.20	>99	93
Poly(**1e**)	7.3	3.2	15	34	1.64	>99	90

[a] The polymers were synthesized by injecting HG2 into a THF solution containing the corresponding monomer. [b] The M_n and $Đ$ values were determined by GPC against poly(styrene) standards in THF. [c] The theoretical M_n values were based on the $[\mathbf{1}]_0/[HG2]_0$ feed ratio. [d] The feed ratio of monomer to catalyst is expressed in terms of the polymer repeat unit. [e] The degree of polymerization was calculated by dividing the $M_{n\ exp.}$ value by the molecular weight of the corresponding repeat unit. [f] Determined using ^{1}H NMR spectroscopy by monitoring the signal (6.2–6.3 ppm; CD_2Cl_2) that corresponded to the respective monomer **1**. [g] Isolated yield (%) after collection of the solids that precipitated after pouring the crude reaction mixtures in cold methanol. [h] Due to its high solubility, the purification of poly(**1c**) was achieved *via* filtration thorough acidic alumina.



Scheme 3 Synthesis of substituted poly(acetylene)s.

polymer) was added to a solution of poly(**1c**) (1.0 mg polymer per mL THF) at 30 °C. A color change from pale brown to red along with the formation of a precipitate was observed after 10 min. The precipitated solids were isolated *via* filtration, and subsequently determined by ^{1}H NMR spectroscopy and mass spectrometry to be triethylammonium chloride ($Et_3NH^+Cl^-$) (see Fig. S13†). After 5 h, the reaction mixture was filtered through a 0.2 μm pore size syringe filter to remove the residual ammonium salt, concentrated under reduced pressure, and then poured into excess cold methanol. The solids that precipitated from the aforementioned mixture were subsequently collected and characterized.

As shown in Fig. 2a, the Raman spectrum recorded for the isolated material (**7c**) featured signals that were assigned to C–C (*ca.* 1163 cm^{-1}) and C=C bonds (*ca.* 1502 cm^{-1}), in agreement with data reported for poly(acetylene);[58] for comparison, these signals were absent in the Raman spectrum obtained for the starting material. Likewise, the UV-vis spectrum recorded for the polymer obtained after the post-polymerization modification exhibited a λ_{max} at 360 nm in THF (ε = 3287.5 M^{-1} cm^{-1})[59] whereas the starting material primarily absorbed light that was relatively higher in energy (Fig. 2b). FT-IR spectroscopy revealed that **7c** exhibited a lower carbonyl stretching frequency ($\nu_{C=O}$) when compared to poly(**1c**) (1720 cm^{-1} *vs.* 1731 cm^{-1}, respectively) and the former lacked the ν_{C-Cl} signal (818 cm^{-1}) found in the starting material (Fig. 2c). Similarly, ^{1}H NMR spectroscopy revealed that the methine protons geminal to the chloro (δ 4.5–5.2 ppm) and the carbonyl (δ 3.1–3.8 ppm; CD_2Cl_2) groups in poly(**1c**) were absent in the spectrum recorded for **7c**; instead, broad signals corresponding to a poly(acetylene) backbone (δ 5.5–8.5 ppm, CD_2Cl_2) were observed (Fig. 2d).[60] Further support for the change in composition was obtained using X-ray photoelectron spectroscopy (XPS) as survey spectra recorded for **7c** showed relatively weak chlorine 2p signals when compared to those present in poly(**1c**) (see Fig. S8†). Collectively, these data indicated that the elimination reaction proceeded to a high conversion and afforded a conjugated polymer.[61]

Additional support for the aforementioned elimination reaction was obtained using GPC. As shown in Fig. 3a, poly(**1c**) and its eliminated derivative exhibited similar chromatograms when visualized using a refractive index detector. However, as shown in Fig. 3b, only the eliminated product (**7c**) was observed when the separation process was visualized with a UV-vis detector (λ_{max} = 360 nm). Moreover, the peak retention volume determined with a UV-vis detector matched the value recorded with the refractive index detector. Since poly(**1c**) does not possess a chromophore, the appearance of a UV-signal following the elimination reaction confirmed the formation of a conjugated structure.

The elimination reaction was quantified using ^{1}H NMR spectroscopy. Signals assigned to the terminal methyl groups of the pendant 2-ethylhexyl substituents (δ 0.7–0.9 ppm, CD_2Cl_2, 6H) were compared with signals that were assigned to the triethylammonium chloride byproduct (δ 3.0–3.1 ppm, CD_2Cl_2, 6H). A ratio of 1.0 was measured after 12 h when 1.0 equiv. of TEA relative to the repeat unit of poly(**1c**) was used, indicating that the reaction had reached completion. Additional experiments involving excess and sub-stoichiometric amounts of TEA provided further confirmation that the reaction was quantitative. For example, a ratio of 1.0 was determined when excess TEA (2.0 equiv.) was added, whereas 0.5

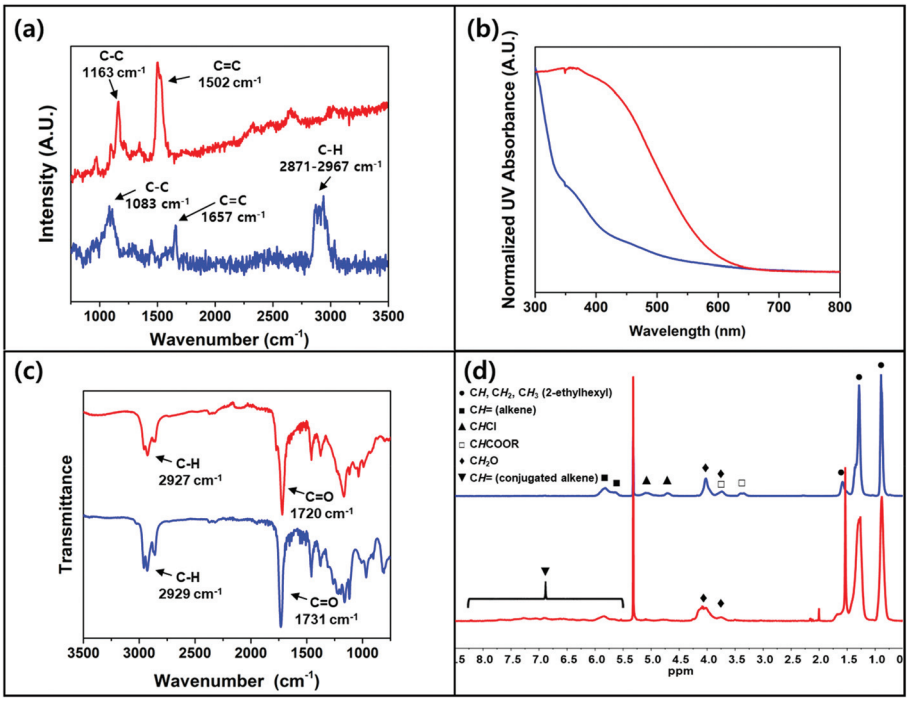


Fig. 2 Summary of characterization data. (a) Raman spectra recorded for poly(**1c**) (blue) and **7c** (red). (b) UV-vis spectra recorded in THF for poly(**1c**) (blue) and **7c** (red). (c) Infrared spectra recorded for poly(**1c**) (blue) and **7c** (red). (d) ^{1}H NMR spectra recorded for poly(**1c**) (blue) and **7c** (red) in CD_2Cl_2.

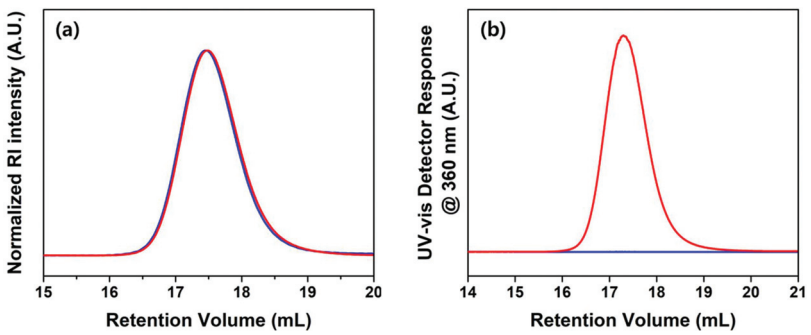


Fig. 3 (a) Representative gel permeation chromatograms recorded for poly(**1c**) (blue) and its eliminated polymer **7c** (red) as visualized using a refractive index (RI) detector. Conditions: $[\mathbf{1c}]_0/[Ru]_0$ = 82, CH_2Cl_2, room temperature; M_n = 24.9 kDa, $Đ$ = 1.17 (blue); eliminated product **7c**; M_n = 23.8 kDa, $Đ$ = 1.19 (red). (b) Representative gel permeation chromatograms recorded for poly(**1c**) (blue) and the eliminated polymer product **7c** (red; M_n = 18.8 kDa, $Đ$ = 1.21) as visualized using a UV detector at 360 nm. Note: Poly(**1c**) and **7c** were prepared at the same concentration (0.5 mg of polymer per mL of THF).

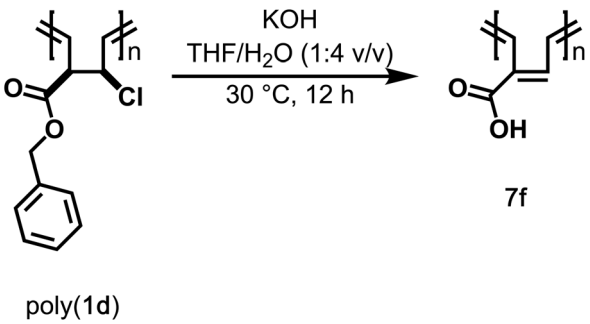
equiv. of TEA resulted in a ratio of 2.0 after the reaction was allowed to proceed for 12 h. Quantitative conversions and relatively short reaction periods (5 h) were realized when 10 equiv. of TEA was used and the reaction was performed at 30 °C.

Using the conditions optimized for the aforementioned elimination reaction, poly(**1a**), poly(**1b**), poly(**1d**), and poly(**1e**) were independently converted to their corresponding poly(acetylene) derivatives (**7a–e**) in yields that ranged from 73 to 98%. UV-vis spectroscopy revealed that each polymer exhibited a λ_{max} value in THF (*e.g.*, **7a**: 322 nm; **7b**: 365 nm; **7d**: 414 nm; see Table S1†)[62] that was dependent on the nature of the ester alkyl substituents. While the optical property differences may be due to the relative electronic coupling interactions between the ester groups and the corresponding polymer backbones, steric effects *vis-à-vis* differential macromolecular conformation may also play a significant role. For example, Masuda and coworkers reported that poly(acetylene) derivatives with ester substituents on every other carbon atom of the polymer repeat unit exhibited relatively low λ_{max} values (*ca.* 325 nm) due to twisting of the polymer chain in a manner that effectively disrupts the electronic delocalization across the conjugated backbone.[40] Juxtaposed are the poly(acetylene) deriva-

tives reported by Grubbs and coworkers which feature repeat units of one pendant group per eight carbon atoms and relatively high λ_{max} values (>500 nm).[31] In comparison, the substituted poly(acetylene)s **7** described herein exhibit intermediate substituent densities and λ_{max} values.

It was previously demonstrated that the quaternization of poly(3-ethynylpyridine) using bromo- or iodomethane resulted in poly(acetylene) derivatives that were found to be soluble in aqueous media.[63,64] Since such types of polymers have potential biological applications,[65] methods to enhance the solubility of the substituted poly(acetylene)s described herein were explored. It has been reported that activated esters, including 2,2,2-trifluoroethyl derivatives, facilitate post-polymerization modifications;[66] as such, we hypothesized that the use of a hydroxide would afford a water-soluble derivative of poly(acetylene) *via* elimination and hydrolysis (Scheme 4).

After treating a THF solution of poly(**1d**) to an aqueous solution of potassium hydroxide (40 equiv. based on the repeat unit of poly(**1d**)), the resulting mixture was slowly added to an aqueous solution of HCl (1 M), which induced precipitation. The precipitated solids were separated from the mother liquor *via* centrifugation, labeled as **7f**, and later determined to be soluble in CH_3OH as well as in basic aqueous media. The FT-IR spectrum recorded for the product featured a strong ν_{O-H} (3000–3700 cm^{-1}) and a relatively weak $\nu_{C=O}$ (1568 cm^{-1}) (see Fig. 4a). Moreover, the ν_{C-Cl} signals observed in the spectrum obtained for the starting material (813 cm^{-1}) were absent in the spectrum recorded for **7f**. The product also strongly absorbed light at a relatively long wavelength (λ_{max} 395 nm, ε = 969 M^{-1} cm^{-1}; CH_3OH) when compared to the starting material, as determined using UV-vis spectroscopy (see Fig. 4b). Consistent with the XPS survey spectrum recorded for **7f** which showed weak chlorine 2p signals, elemental analysis data agreed with its theoretical composition (see Fig. S8 and Table S3†). From these results, we concluded that the structure of the water-soluble polymer material featured a conjugated backbone in addition to pendant carboxylic acid substituents.



Scheme 4 Treatment of poly(**1d**) with base afforded the water-soluble poly(acetylene) derivative **7f** *via* concurrent elimination and hydrolysis.

A similar transformation was performed by treating a THF/H_2O solution (3 : 1 v/v) of poly(**1e**) with LiOH (8.2 equiv. per repeat unit). After allowing the reaction to proceed for 12 h at 30 °C, the solution was acidified using an aqueous solution of HCl (1 M), which formed a dark red precipitate. Although the precipitate was found to be insoluble in neutral water, enhanced solubilities were realized in aqueous solutions that were saturated with sodium bicarbonate, which may facilitate deprotonation of the pendant carboxylic acid groups and drive the dissolution of the polymers. The isolated precipitate contained relatively minimal amounts of chlorine (<1 atomic%) when compared to the starting material, as determined by XPS, and exhibited spectroscopic signals that were similar to the polymer product obtained from poly(**1d**) (*i.e.*, **7f**).

As noted above, the monomers utilized throughout this study did not undergo polymerization when subjected to the G3 catalyst.[67] The result was unexpected and the origin of the inactivity was probed. Multiple signals were observed in the region of the ^{1}H NMR spectrum where Ru benzylidenes are typically observed (δ ~20 ppm) when a crude reaction mixture containing a 1 : 1 molar ratio of **1c** and G3 in CD_2Cl_2 ($[\mathbf{1c}]_0$ = 0.4 M) was analyzed by ^{1}H NMR spectroscopy. For comparison, an analogous experiment performed with HG2 resulted in the formation of a single signal that was recorded downfield from a signal attributed to the benzylidene of the catalyst (18.3 ppm *vs.* 16.5 ppm, respectively; CD_2Cl_2). The observation of multiple signals in the former experiment may reflect the formation of distinct species,[68] some of which may be catalytically-inactive.

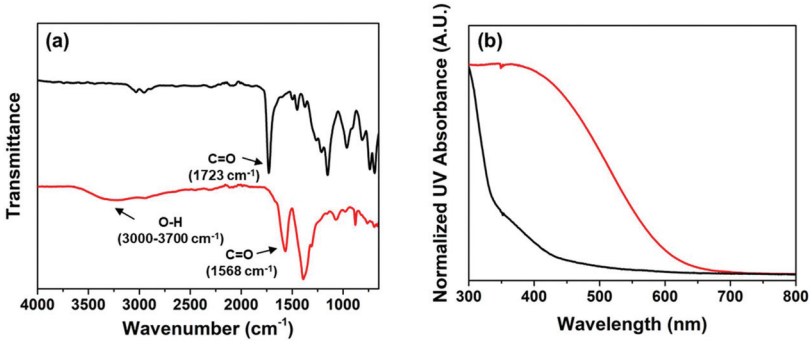


Fig. 4 Summary of spectroscopic data. (a) Infrared spectra recorded for poly(**1d**) (black) and polymer **7f** (red). (b) UV-vis absorption spectra recorded for poly(**1d**) (black) and polymer **7f** (red). Conditions: $[\text{Poly}(\mathbf{1d})]_0$ = 1.1 × 10^{-2} mg mL^{-1} in THF; $[\mathbf{7f}]_0$ = 1.3 × 10^{-2} mg mL^{-1} in CH_3OH (in terms of repeat unit).

Since G3 is supported by pyridines, we hypothesized that the bases liberated during the initiation step of the catalytic cycle were impeding the polymerization reaction. To test this hypothesis, a stoichiometric mixture of HG2 and **1c** was combined with 3-bromopyridine (2.0 equiv. relative to the catalyst) and stirred for 2 h. Although ^{1}H NMR analysis of revealed the formation of a new, single signal (18.3 ppm; CD_2Cl_2), the introduction of additional monomer did not result in a polymerization reaction. As such, we surmised that the added base was arresting the catalytically-active species. To determine if the basicity of the added pyridine played a role, different pyridine derivatives were explored. Polymerization was not observed when 3-bromopyridine, 2-isopropylpyridine, or other relatively strong bases were used. In contrast, polymerizations were found to proceed smoothly in the presence of relatively weak bases (*e.g.*, 2-fluoropyridine, 2-cyanopyridine, or 2-nitropyridine) (see Table S2†). Likewise, polymerization was observed when tetrafluoroboric acid (2.0 equiv. relative to the added catalyst) was added to a reaction mixture containing a mixture of **1c** and G3 ($[\mathbf{1c}]_0:[G3]_0 = 100$; $[\mathbf{1c}]_0 = 0.2$ M in CH_2Cl_2). We reasoned the liberated 3-bromopyridine was quenched by the acid, which effectively prevented it from interacting with the active metal center.

Based on the aforementioned results, we propose that relatively basic pyridines effectively arrest the active catalyst *via* the formation of an enolate intermediate (**8**) (see Fig. 5). Data consistent with the proposed structure was obtained upon high-resolution mass spectrometric analysis of a crude reaction mixture collected after subjecting a CH_2Cl_2 solution of **1c** ($[\mathbf{1c}]_0 = 0.2$ M) to G3 (**1c** : G3 = 3.0) in the presence of excess 3-bromopyridine (10 equiv.) for 12 h (calcd for $[M - Cl]^+$: 898.2282; found: 898.2279, see Fig. S41†).[69,70] Further confirmation was obtained by analyzing the reaction mixture using FT-IR spectroscopy which revealed that the salient $\nu_{C=O}$ signal of the monomer underwent a significant reduction in intensity over the course of the reaction (see Fig. S6†). The proposed structure of the arrested catalyst, which features a 3-bromopyridine ligated to the metal center, was also borne through experiment: adding one equivalent of 3-bromopyridine relative to HG2 was insufficient to inhibit the polymerization of **1c** whereas catalytic activity effectively ceased when two or more equivalents were used. Since the arrested catalyst did not appear to be paramagnetic, it was assumed to be in the Ru(II) oxidation state and therefore may be negatively charged in solution. Literature precedence for the assignment include reports of O-bound enolate Ru complexes[71] and carbonyl-stabilized intermediates[72] that exhibit relatively low catalytic activities. Likewise, O-chelation was also hypothesized to attenuate the activity displayed by Ru complexes during the ROMP of mono-substituted cyclobutenes.[73]

Conclusions

A series of alkyl 4-chlorocyclobut-2-ene-1-carboxylates were readily prepared from Dewar lactone and polymerized with the Hoveyda–Grubbs 2nd generation (HG2) catalyst. The ring-opening metathesis polymerization reactions proceeded in a manner that was controlled and also enabled chain extensions. The high degree of control over the polymerizations was unexpected since HG2 often suffers from poor initiation characteristics. For comparison, polymerizations that were performed with G3 were impeded by a basic ligand (3-bromopyridine) that dissociates during catalyst initiation. Treatment of the aforementioned polymers with an organic base (*e.g.*, triethylamine) afforded poly(acetylene) derivatives that featured

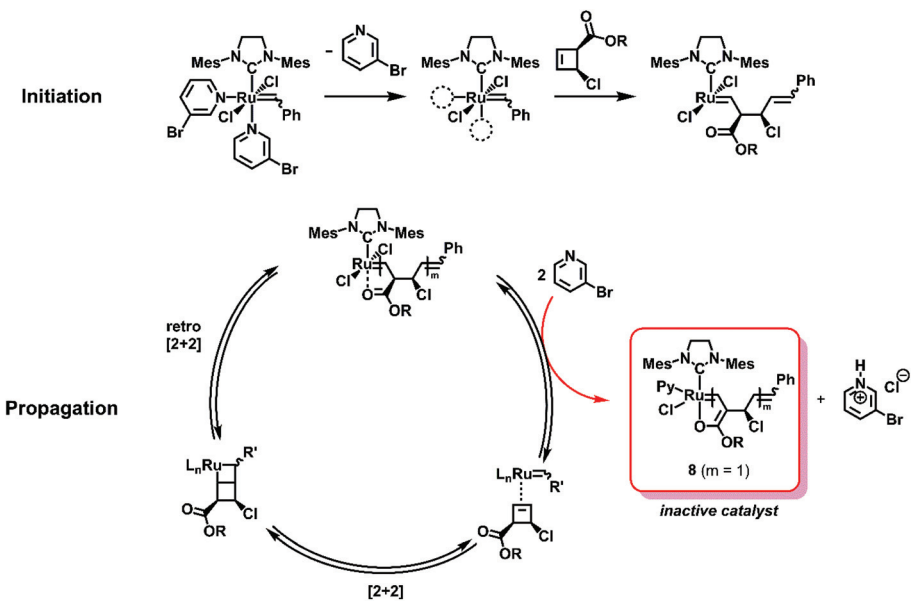


Fig. 5 A proposed mechanism that rationalizes how base (*e.g.*, 3-bromopyridine) may disrupt a catalytic cycle. Py = 3-bromopyridine. R = 2-ethylhexyl. R′ = growing polymer chain.

substituents on every fourth carbon atom of the repeat unit. The pendant substituents enhanced the solubility of the polymers while altering their intrinsic electronic properties. Water-soluble derivatives were also realized. The methodology described herein not only favorably compares to other post-polymerization modifications that utilize elimination chemistry to form conjugated polymers[74–76] but establishes a new approach to poly(acetylene) derivatives with tunable solubilities, molecular weights, and electronic properties.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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